

Interactive comment on “High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels” by Kanako Sekimoto et al.

Anonymous Referee #1

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This paper presents results of positive matrix factorization (PMF) analysis on data collected with a Proton Transfer Reaction Mass Spectrometer (PTR-MS) during laboratory burns of various wildfire fuels during the FIREX campaign. The data set, describing VOCs and other volatile components (e.g. NH₃), was described in another publication, and here the authors use PMF to show that much of the variability in emission profiles across and within burns can be explained by two factors, which they associated with high- and low-temperature pyrolysis processes. They show that a single pair of factors can explain the variability in most burns nearly as well as fuel/burn-specific factors, with

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a few exceptions (e.g. rotten wood, duff). They then included a detailed dive into the two factors, including: the absolute and relative contributions of different compounds, function groups represented in each, and their estimated OH reactivities and volatilities. The paper also emphasizes that modified combustion efficiency (MCE), often used to parameterize combustion types and VOC emission profiles, does not capture the pyrolysis-temperature-driven variability captured here, suggesting that it is not a good proxy for varying emission conditions.

This is really nice paper, which makes excellent use of this interesting data set to put forward a compelling case for the importance of pyrolysis temperature on dictating the mixture of VOCs emitted from biomass combustion. This is a topic of great interest, as wildfire VOC emissions (and their variability across fires, space and time) are important and poorly constrained inputs for atmospheric models. The analysis is thorough, cutting across a multi-dimensional data set in a logical way, and the paper is clearly written and includes highly informative figures. Therefore, this paper is highly suitable for publication in ACP. Below, I list a number of questions and minor concerns that I would like to see addressed before the paper's final publication. Most are clarifications, though a number of points are suggestions for additional steps that the authors may wish to take to enhance the impact and usability of their findings in the broader community interested in biomass burning impacts on the atmosphere.

General comments

Although it was eventually clear, I found the initial attribution of factors to high- and low-temperature pyrolysis processes to be a bit confusing. I think it might be helpful to move Fig. 4b and some more background discussion of combustion processes to the introduction of the paper. There is currently a nice brief introduction (e.g. L60-71), but then the importance of pyrolysis temperature on VOC composition isn't really discussed into well after results are presented (i.e. after discussion of Figs. 1-3). As it is, this feels like a 'grand unveiling' of something that would be better described earlier. For example, line 94 calls high and low-T pyrolysis the 'main processes (sic) of the

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VOC emissions from biomass burning' without a reference – if this is so, shouldn't that be made clear earlier, with specific references and summary of what is known about VOC emission as a function of pyrolysis temperature outlined early on? This point is also strongly made on Lines 232-234 without much specific justification.

Some of the description of VOC quantification is a bit unclear. For example – Line 87 says that 90% of instrument signal could be attributed to identified VOCs, but then on lines 159 and 160 it is stated that 'many ion masses cannot be unambiguously related to a single VOC contributor... and cannot be converted to a mixing ratio'. I assume this is because most of the overall signal is due to a relatively small number of compounds, but perhaps this can be clarified a bit – e.g. how many compounds are actually quantified as mixing ratios? Also, can you estimate approximately what fraction of total emitted NMVOC your measurements represent?

The use of the Pearson's correlation coefficient (r) doesn't really seem appropriate since you are actually presenting regression results (slopes) not correlations alone. Also, the Figure 2 caption states that r was calculated based on log-transformed normalized signals, were slopes also calculated this way? This should be done consistently and described clearly. I'm not an expert statistician, but it seems that there may be a better way to compare factors – as it is, you are using difference in r values between 0.91 and 0.83 (for example) to say that factors are quite similar or quite different (Fig. 2d and 2e). I wonder if there are better ways to contrast the spectra than is presented here?

As noted in a few places, one of the major drivers for VOC speciation is to understand SOA formation potential, but the final step to that isn't taken. As stated (L 398) yields are an important missing piece here, other similar papers on biomass combustion has taken that step (Bruns et al. 2016, 2017). The authors could consider adding some kind of scoping analysis to this paper, or certainly extending this in future work with this dataset.

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One of the main reasons that MCE appeals as a proxy for combustion conditions is that it is based on easily-measurable quantities (including from satellites). While you may point out its limits here, it would be great if (relatively) simple alternatives were proposed/discussed. For example, are there any especially robust 'marker species' for the two factors across all fuel/burn types? For example, Cresol and guaiacol seem to be distinct features of high and low T factors with substantial contributions (Fig. 2), but perhaps there are others that are more consistent. Could the ratio of these two serve as a proxy for relative factor strength? How can this approach be simplified to be applied by different analytical approaches or other data sets? Does MCE have any explanatory power for relative factor strength across your data set or in some subsets? Are there any other emission ratios (especially for species that are frequently measured, especially by remote sensing) that do?

Specific points:

Lines 239-243 – This point seems like it could use a bit more justification. To my eye, the addition of a third factor in Fig. S2 does seem to make a pretty substantial difference – there is quite a bit of scatter in the fit vs. reconstructed Factor 3 time series plot (bottom right). Is there a way to make this point more convincingly?

Line 337-339 – This is a bit confusing/misleading – pyrolysis will still happen during flaming combustion as there is heat transfer from the flame to surrounding biomass. As you state elsewhere, all of these processes are happening simultaneously in most cases. Therefore, it might be expected that the dominance of different factors might be linked to flaming- versus smoldering-dominated burns or stages of a burn.

Line 232 - should be 'make a higher contribution in the low-T factor', I think?

Line 391-392 – This doesn't seem necessary considering that your estimated OH reactivities for the two factors are basically identical. This is a nice result, that suggests that OH reactivity scales directly with NMVOC (for the compounds you've detected). Seems like something to note.

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Section 3.3.3 – It would seem more appropriate to show this distribution on a mass (versus molar) basis, as is typically done for volatility basis set representations. As noted above, yields could be approximated to take the next step, which would be very helpful but not necessary.

Line 445 -450 – I see this is true across fuel/burn types, but what about within a burn? Are there any stages in which transitions in MCE map to transitions in factor-strength? The time-series discussed here shows CO/CO₂ for the rotten pine case (Fig. S6), but that doesn't seem like an appropriate example as it is pretty much dominated by the low-T factor (I can't visually average these two. . .). Having some time series plots with MCE during a burn along with the factor contributions (possibly a separate trace on Fig. 1) would address this better. Is there any correlation between MCE and the relative contribution from the different factors during burns?

Line 558-560- Residuals from PMF fitting are not really discussed elsewhere in the paper. They either should be or the effectiveness of fitting discussed in another way here.

Figure 4b – Would like a more detailed caption. What do color bars correspond to - just temperature ranges? Why does the red bar span a wider temperature range for lignin?

References

Bruns, E. A., El Haddad, I., Slowik, J. G., Kilic, D., Klein, F., Baltensperger, U., and Prévôt, A. S. H. (2016). "Identification of significant precursor gases of secondary organic aerosols from residential wood combustion." *Scientific Reports*, 6, 27881.

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